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CONCENTRATION BY reverse osmosis OF MAPLE SAP

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■ IN MAKING maple sirup, sap must be concentrated 25- to 30-fold. The customary method of doing this is evaporation by boiling at atmospheric pressure until the solids content reaches 65.5° Brix. This evaporation is one of the most expensive of the different steps involved in maple sirup production, and is now done by boiling off the water in open-pan thermal evaporators. Fuel cost ranges from 45¢ to 55¢ per gallon of sirup, depending on the efficiency of the operation. For this reason, economical new methods of sap concentration are constantly being sought.

In the following we report how the principle of reverse osmosis can be used to effect removal of 75% of the water that must be removed to concentrate maple sap to standard density sirup. The energy cost of this concentration by reverse osmosis is only a fraction of that for water removal by heat.

BACKGROUND

RECENTLY (Mangan and Shackelford, 1964), attention has been directed to obtaining pure or potable water from sea or brackish water by reverse osmosis. Application of this principle of water removal from solution led to the work of A. I. Morgan, Jr. and coworkers (1965) on the concentration of fruit juices and to the work described here on the concentration of maple sap.

Reverse osmosis is a process by which water is caused to flow through a semipermeable membrane but in a reverse direction to that in which it moves in normal osmosis. Osmosis occurs when two solutions of different concentrations, but in the same solvent, are separated by a membrane permeable to the solvent but not the solute. The solvent passes through the membrane to the more concentrated solution. If the concentrated solution is in a chamber of fixed dimensions the flow of solvent through the membrane into this concentrated solution will continue until an equilibrium pressure inside the chamber is obtained. This pressure is termed the osmotic pressure. If a pressure in excess of the osmotic pressure is applied to the more concentrated solution, water is caused to flow through the membrane to the more dilute solution. This reverse flow is termed reverse osmosis.

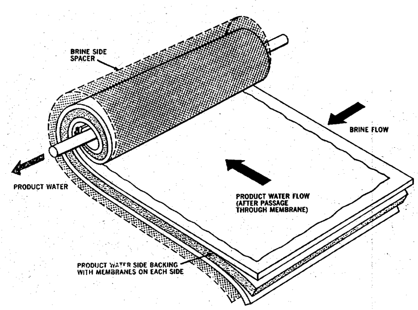

FIG. 1. *Partially assembled module to show its structure.*

In 1953 at the University of Florida, a program was initiated under the direction of C. E. Reid and supported by the Office of Saline Water, U. S. Department of the Interior, to study reverse osmosis as a desalinization method. During the intervening 13 years, there has evolved a semipermeable membrane system suitable for the removal of water from aqueous solutions by reverse osmosis. This has resulted largely from investigations conducted by C. E. Reid and E. J. Breton (1959) and S. Loeb and S. Sourirajan (1963). U. Merten (1965) has recently summarized the progress made by these and other investigators toward an appreciation of some of the practical problems associated with reverse osmosis as a desalinization process; an understanding of the transport phenomena which occurs in the osmotic membrane, particularly in cellulose acetate; and a description of the formation, structure, and properties of cellulose acetate membranes.

Since maple sap is a single-phase system consisting of a dilute solution of sugar (1–5%) together with small amounts of organic acids and acid salts, it was assumed that at least part of the water of the sap could be removed by reverse osmosis, employing the same cellulose acetate membrane, backing, and assembly that were developed for the desalinization of sea water. However, since in maple sap concentration the desired product is the concentrate and not the "pure" water, two important facts had to be established. One was the effect of this process on the flavor of the sirup made from sap concentrated by reverse osmosis. The other was the extent of the loss of sugar or other sap solids through the semipermeable membrane.

It has been established that maple sap does not contain maple flavor *per se* but only substances that are precursors of flavor which are caused to interact during its heat treatment while being concentrated to sirup by boiling (C. O. Willits and W. L. Porter, 1950). Therefore, none of these precursors of maple flavor should pass through the membrane into the separated water since to do so would affect the flavor in the resulting sirup. Likewise, a loss of only 1% of the sugars of sap in the by-product water (the water removed from the sap) would make the application of this process to sap concentration uneconomical.

EXPERIMENTAL

PRELIMINARY TESTS using the modified cellulose acetate films, complete with backing, made up as units in a "module" (D. T. Bray, U. Merten, and M. Augustus, 1965) showed that the obtained maple sap concentrate, when converted to sirup by the conventional heat evaporation process, had the full maple flavor. Likewise, these tests indicated that the reverse osmosis had no effect on the subsequently developed color and contributed no foreign or "off" flavors to the sirup. Based upon the promising results of the preliminary experiments the study of sap concentration by reverse osmosis was continued.

Since heat is required for maple fla-

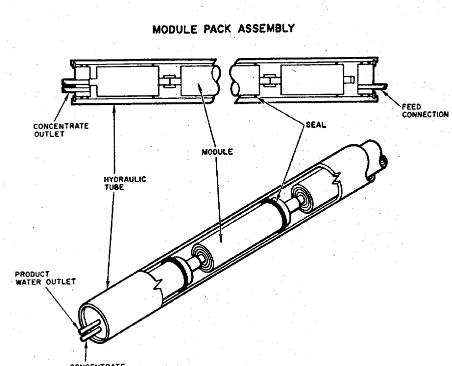

FIG. 2. *Modules mounted in series in a stainless steel tube.*

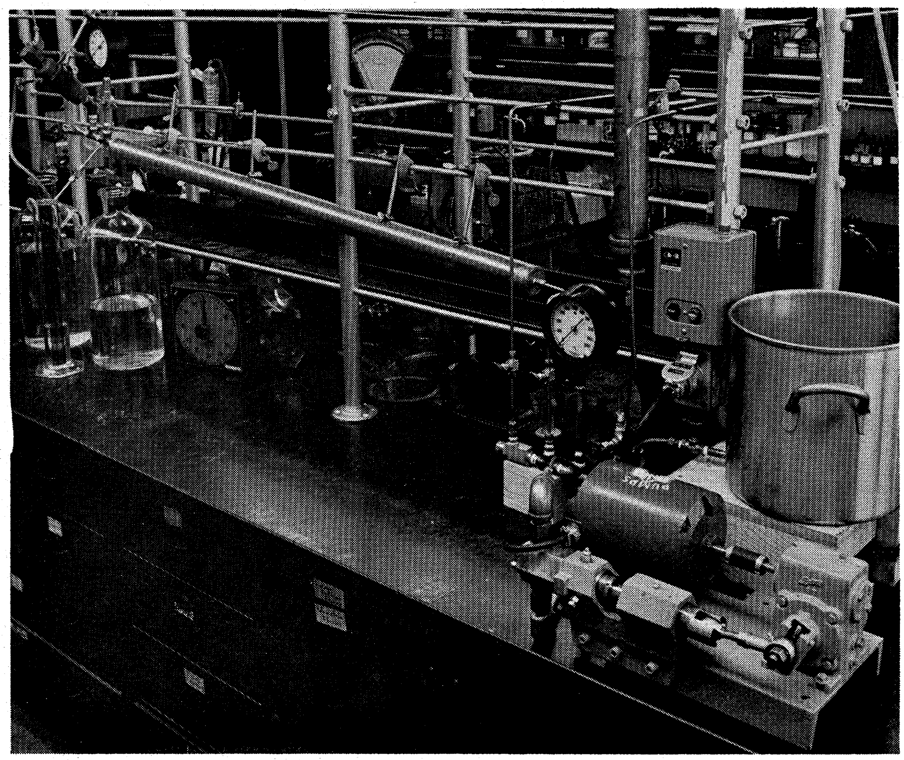

FIG. 3. *The four-module unit used in the experimental work reported in this paper.*

vor development and because it is more convenient to carry out the reverse osmosis process at room or ambient temperatures, it was desirable to remove most of the water (70–80%) by the reverse osmosis process and then remove the remainder of the sap water by the conventional open-pan heat distillation (boiling) method. Fortuitously, the combination of these two methods of water removal from sap are compatible since it has been established that the development of maple flavor and maple color are favored by heating (boiling) solutions of sap concentrated to 40° Brix or above (C. O. Willits, W. L. Porter, and M. L. Buch, 1952). The concentration of sap from its original sugar content of 2.5° Brix to 10° Brix removes 75% of the water in the original sap. The removal of this amount of sap water by reverse osmosis would leave less than 25% to be removed by the conventional heat process. This would provide adequate heating for flavor development.

Four of the cellulose acetate film modules (Fig. 1), supplied by General Dynamics Corporation, were assembled in series in a stainless steel cylinder as shown in Fig. 2. Each module contained approximately 3.7 square feet of active membrane area. Maple sap was pumped through the modules using a high pressure simplex pump, and the pressure regulated with an adjustable relief valve (Fig. 3). The pump yielded a sap feed flow rate of about 1000 ml./min. which was essentially independent of operating conditions. The sap concentrate obtained from pumping sap through the four-module reverse osmosis apparatus was repassed through the system. This was repeated until the desired concentration of sap was obtained. The temperature of the sap was not closely controlled, but ranged between 20° and 25°C during the course of the experiments.

To evaluate the apparatus, the rate of flow of by-product water (sap water that passed through the membrane) was determined at different pump pressures, from 200 to 600 psig, and for sap of different concentrations (degrees Brix). The pH of the by-product water and of the concentrated sap was determined using a glass electrode, line-operated pH meter. The by-product waters obtained for each of the different pressures were analyzed for total solids by drying, for ash by combustion at 600°C, and for sugars by the Berlin method (AOAC, 1965).

RESULTS

THE RATES of flow (recovery) of by-product water (water passing through the semipermeable membrane) through the module system at different pump pressures for sap of different concentrations are given in Fig. 4. Sap of the lowest degrees Brix, when pumped through the system at 600 psig, had the highest by-product water flow rate. With the lowest flow rate occurring at 200 psig, an increase in the Brix of the sap caused a slight decrease in the flow rate of by-product water at the higher pump pressure but no measurable effect at 200 psig.

The change in flow rate of by-product water from sap through the four-membrane modules system as shown in Fig. 5 was directly proportional to the pressure, with the highest rate of approximately 500 ml/min. at 600 psig and the lowest rate of 100 ml/min. at 200 psig. *(more)*

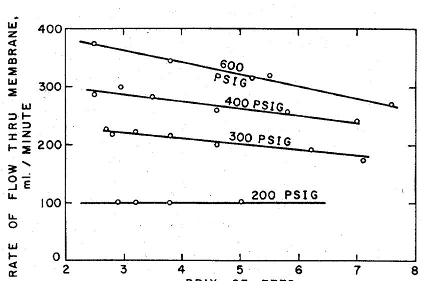

FIG. 4. *Rate of flow through membrane with change in Brix of feed at different pressures.*

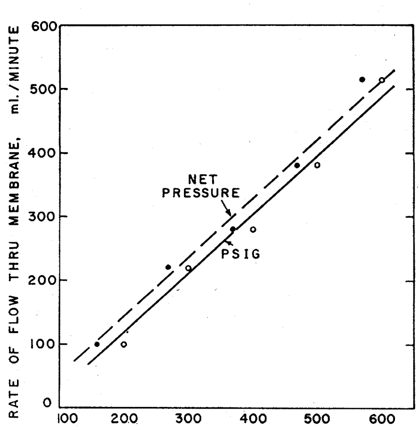

FIG. 5. *Change in flow rate through the membrane with increase in pressure.*

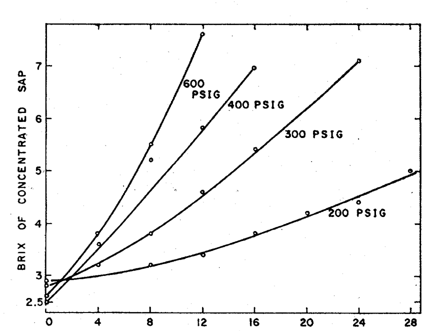

FIG. 6. *The change in Brix of the concentrated sap as the number of modules through which it passed increased at different pressures.*

Table 1. Sap solids in product water.

Operating pressure (psig)	Total solids mg/100 ml
400	0.3
500	0.3
600	0.09

Example: In the production of 2,000 gallons of sirup there is a loss of only 1 gallon.

The increase in concentration, degrees Brix, of the sap passed through increasing numbers of membrane modules and under different pressures is shown in Fig. 6. The sap concentration occurred most rapidly, of course, when it was pumped through the system at 600 psig. As the pump pressure diminishes, greater numbers of modules are required to produce an equal concentration of sap at a constant feed rate.

The change in pH of sap with changes in its concentration is shown in Fig. 7. There is a small but positive change from 6.8 (the pH of the raw sap) to 7.1 obtained after the sap had been passed through the four-module apparatus six times. The smallest change in the pH of the concentrated sap occurred at the highest operating pressure.

The analysis of the by-product water, sap water passing through the cellulose acetate member of the modules at different pressures, is given in Table 1. Only a trace of sap solids passed through the membrane with the by-product water. The least amount was 0.09 mg/100 ml, obtained with pump pressures of 600 psig. These solids contained 30% sugars and 3% ash.

DISCUSSION

As EXPECTED, the rate of water passing through the semipermeable membrane was greatest at the highest pump pressures, which confirmed the work of others (U. Merten, 1965) that the amount of by-product water is proportional to the net pressure applied, where the net pressure is defined as the applied pressure minus the osmotic pressure of the sap. On this basis, one would expect flow rates to be more highly dependent on concentration at low pressures, where the fractional change in net pressure caused by a given concentration change is greatest, than at high pressures. The fact that Fig. 1 indicates the opposite result is probably attributable to the occurrence of sharp concentration increases at the membrane-solution interface due to boundary layer effects occurring at the highest permeation rates, i.e. at the highest pressures.

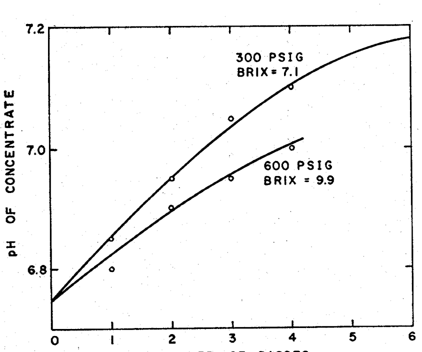

FIG. 7. *Change in pH of the sap with increasing number of passes through the four-module unit.*

Fig. 6 shows that the higher the pressure the fewer the number of modules (less equipment) required to effect a given sap concentration at a given feed rate. The major limiting factor for efficiency of operation is the pressure which the semipermeable membrane of the modules will withstand without danger of rupture or permeability loss.

The amounts of sap solids passing through the membranes did not follow a well defined pattern with pressure. One would expect that the amount per unit time would be relatively independent of the pressure, but would depend upon time and concentration. Therefore, it is desirable that the greatest amount of water be removed from the sap in the shortest possible time. This requirement is met by utilizing the maximum allowable pressure at which the sap can be pumped through the system. The loss of solids data (Table 1) show that about 1 part in 2 thousand of sap solids were lost in the by-product water. This is much less than other losses encountered both in maple sap harvesting and in its conventional processing to sirup.

For obtaining potable water from sea water a ratio of 20 volumes of feed to 1 volume of product water has been found to be desirable for the efficient operation of the reverse osmosis system. This ratio was found to provide a rate of flow of concentrated solution across the surface of the cellulose acetate membranes sufficient to keep them washed free of deposit. In our experiments, the simplex pump produced a ratio of 8 volumes of sap concentrate to 1 volume of product water. This ratio provides for high economy of operation since it reduces appreciably the number of modules and supporting equipment required to obtain the desired concentration of sap. However, an increase in pumping rate should increase by-product water flow and decrease solids loss.

The only energy required for removal of water from sap by reverse osmosis is the electric energy to operate the pump. The production of 1 gallon of sirup would require pumping about 30 gallons of sap to, say, 600 psi. Assuming 75% pump and motor efficiency, this requires only 0.09 kwhr, which can be purchased for about 0.2 cents at usual electricity rates. Based upon approximate cost estimates, the reverse osmosis apparatus will be slightly more expensive than the conventional thermal evaporation equipment, but this cost should be offset by the much cheaper operation of the reverse osmosis equipment.

Based upon these experiments a pilot plant reverse osmosis sap concentration plant will be built and operated during the 1967 maple sap flow season. This will provide operational data that is not now available.

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